Molecular Dynamics Simulations of Force Fields for Modeling Crystalline SiO_2

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Introduction. Silica is among the most abundant materials on the planet and is used in the fabrication of computer wafers and microprocessors, the development of advanced instrumentation for diagnostics and data acquisition devices in research, and many medical and industrial applications including photonics, nuclear-targeted drug-delivery, fused silica optics, and micro/nano-electronics as nano-composite films, blue-light emitters, and waveguides. The interface of silica with silicon, water, and oxygen is also of interest for transistor development, chromatography, and atomic oxygen collisions, respectively. Characterizing silica at the atomic scale can help predict the behavior of silica under various conditions, as opposed to a more expensive experimental approach.

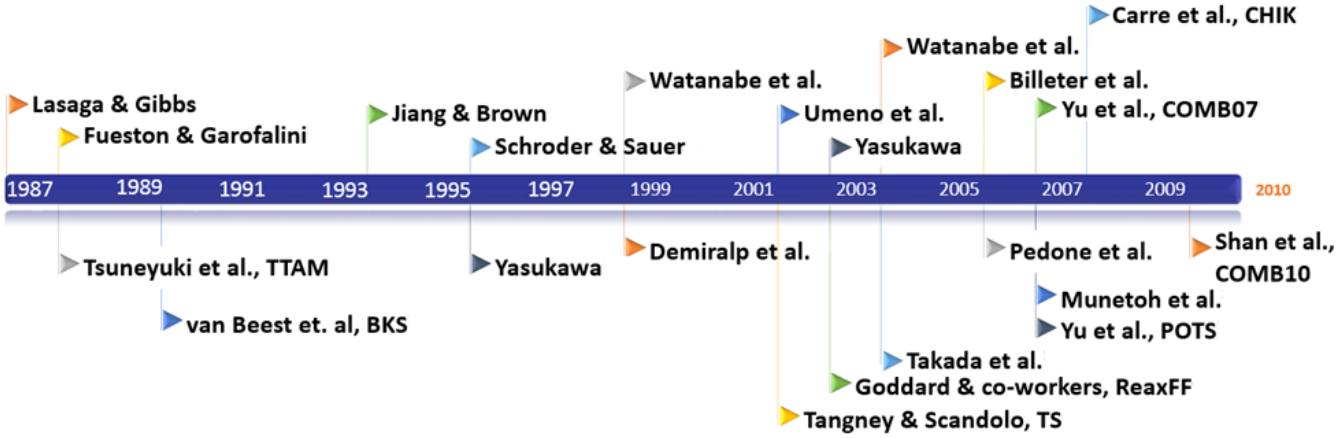

Figure 1: Timeline since 1987 of some of the MD simulation potentials for explicitly modeling silica.

Molecular dynamics (MD) simulations have been highly recognized for the ability to effectively describe the atom-atom interactions, with successful applications to all sorts of materials, including carbon nanotubes, biomolecules, hydrocarbons, and metallic oxides to name a few. Several potentials have been developed that attempt to provide a sounds physics model of the atomic interactions in silica (Fig. 1), which can be described as covalent and ionic. The computational cost, accuracy, and transferability of 8 interatomic potentials have been investigated to determine the most suitable one throughout the phase diagram. The potentials investigated fall into three categories; fixed-charge, two-body (BKS, Pedone, TTAM, and CHIK), no-charge, three-body (Munetoh), and bond-order variable-charge (BOVC), three-body (COMB10, $\mathrm{ReaxFF}^{\mathrm{H_2O}}_{\mathrm{SiO}}$, and $\mathrm{ReaxFF}^{\mathrm{GSI}}_{\mathrm{SiO}}$) potentials. The latter are important for modeling complex chemical reactions and interfaces. All potentials are used to model four polymorphs of crystalline SiO_2, namely, quartz, cristobalite, coesite, and stishovite.

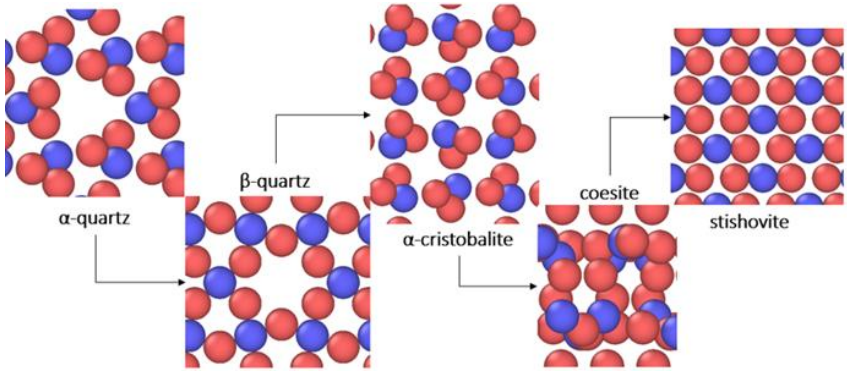

Figure 2: Polymorphs of crystalline silica that are simulated with 8 potentials, using MD simulations.

Modeling and Computational Approach. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), an open source code developed by Sandia National Laboratories, was used to carry out all MD Simulations. The performed MD simulations track the positions and velocities of the atoms by time-integrating the Nose-Hoover style, non-Hamiltonian equations of motion, by sampling from the isothermal-isobaric (NPT) ensemble. The QEq scheme is used to charge-equilibrate the variable-charge potentials, and the particle-particle particle-mesh (PPPM) solver is used for the fixed-charge potentials. A time step of 0.2 fs was used for the BOVC potentials, whereas the rest employed a time step of 1.0 fs. The crystal structures were obtained from Crystallography Open Database. Results are compared to prior work that investigated the potential by Tangney and Scandolo (TS) and a modified DCG (mDCG) potential. The cutoff used for the fixed-charge potentials is 15 Å, unless otherwise indicated.

Results. The BKS potential was shown to be the most accurate for modeling crystalline SiO_2, with the lattice constants, density, and radial distribution functions of the polymorphs to within 2% of experimental values, except cristobalite, which is remedied with a shorter cutoff distance. The quartz α-β and I-II phase transitions were the most accurate with the BKS potential, indicating its accuracy and transferability throughout the phase diagram. The TTAM and CHIK potentials were similar to BKS, but were slightly less accurate. The Pedone potential was also shown to be highly accurate and transferable to many regions of the phase diagram, but was inaccurate for modeling the quartz I-II phase transition. The Munetoh potential is the most efficient in terms of computational cost, but it is the least accurate in predicting many of the crystalline silica structural properties, since it neglects Coulomb interactions. The COMB and ReaxFF potentials were not accurate in predicting the α-β transition in quartz. COMB10 was able to model the structural properties of all polymorphs except cristobalite with reasonable accuracy, and ReaxFF was accurate for modeling the structural properties of all polymorphs except stishovite. The results of the quartz α-β transition and stishovite equation of state for some of the potentials are shown in Figs. 3 and 4, respectively.

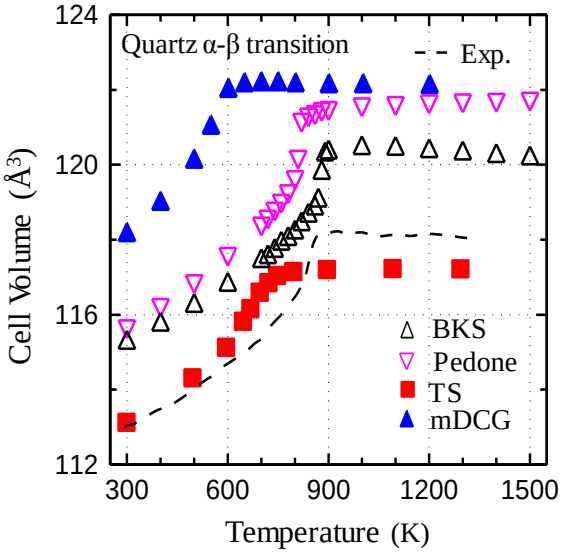

Figure 3: Comparison of the calculated cell volume expansion at the α-β transition of quartz, using different potentials, to experimental measurements.

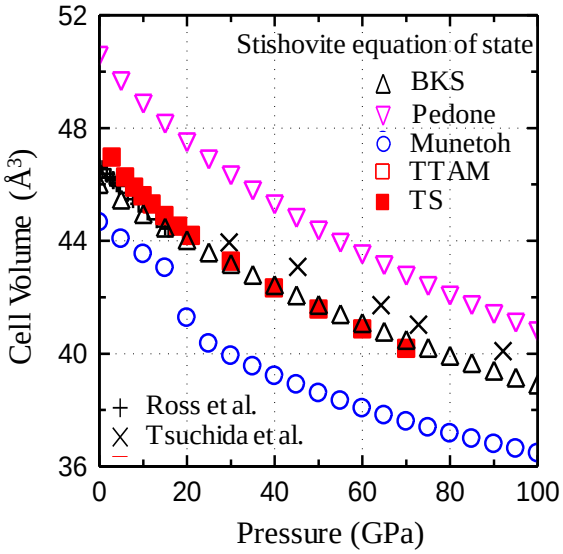

Figure 4: Comparison of the calculated relative cell volume of stishovite at 300 K as a function of pressure, using different potentials, to experimental results.

Closing Remarks. The BOVC potentials, an order of magnitude more expensive than the fixed-charge potentials, should only be used in which BKS and Pedone will not perform as well, such as for complex reactions and interfaces. The BKS and Pedone potentials are the most accurate for modeling the structural properties of silica and the α-β transition in quartz. This work has judiciously tested 8 interatomic potentials for MD simulations of silica, revealing the most suitable potential for a given set of operating conditions.

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